

Analysis of Combustion Chamber Deposits by ESI-TOF-MS and MALDI-TOF-MS

J. G. Reynolds, S. J. Shields, J. W. Roos

This article was submitted to
American Society of Mass Spectrometry, Chicago, IL., May 28- June
1, 2001

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

June 14, 2001

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy
And its contractors in paper from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-mail: reports@adonis.osti.gov

Available for the sale to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-mail: orders@ntis.fedworld.gov
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

Analysis of Combustion Chamber Deposits by ESI-TOF-MS and MALDI-TOF-MS

John G. Reynolds¹, Sharon J. Shields¹, and Joseph W. Roos²

¹University of California, Lawrence Livermore National Laboratory, Livermore CA

²Ethyl Corporation, Richmond, VA 23217

Introduction

Combustion chamber deposits (CCD) in internal combustion engines have been studied by various techniques to understand the relationship of performance degradation with deposit quantity and structure. XPS, XAS, NMR, and elemental analysis have offered insight into the bulk structure of C, H, N, O and metal components. MS has offered some information about compound structure, but results are limited due to the insolubility and complexity of the materials. Recently, we have reported on the metal structure by XPS and XAS of several deposits from a GM 3800 engine generated using a standard fuel and one that contains low levels of the gasoline anti-knock additive, MMT. Here we report the initial findings on the carbon structure of these deposits determined by ESI-TOF-MS and MADLI-TOF-MS.

Methods

One set of CCD samples was taken from a 6-cylinder GM 3800 engine that was operated for 200 h on a standard fuel. The other corresponding set was taken from the same engine after it was cleaned and then operated on the standard fuel containing approximately 12 ppm MMT for 200 h. The samples were soxhlet extracted with a 92 % methylene chloride/ 8% methanol (vol/vol) mixture. The solvent was removed from both fractions. The soluble fraction was dissolved in a methylene chloride/methanol mobile phase and analyzed by ESI-TOF-MS in positive ion mode. The insoluble fraction was analyzed by MADLI-TOF-MS slurried in methanol, but using no matrix. Infrared analysis was performed on both fractions as KBr pellets.

Preliminary Data

IR analyses of the whole deposits show a combination of alkyl and aromatic hydrocarbon features (regions around 2900 and 1600 cm^{-1}) and carbonyl functionality (1600 to 1700 cm^{-1}). The separated fractions show the soluble fraction to have prominent aliphatic and aromatic components with carbonyl functionality, while the insoluble fraction displays prominent carbonyl features and less aromatic features. Little differences are seen among the samples by IR.

The soluble fraction of cylinder 1 deposits from standard fuel operation was examined by ESI-TOF-MS from m/z 200 to 2000. The spectra clearly show several mass series over the entire m/z range. Each component of the series appears to be separated by m/z 72 from the next in the series, much like a hydrocarbon homologous series is separated by m/z 14. Four of these series can be clearly identified with the most intense mass of each of the series being m/z 545.41, 717.575, 601.446, and 703.549, respectively. Examining the region between m/z 545 and 617, peaks are visible at m/z 559, 573, 601,

and 615, all components of other definable mass series where the components are separated by m/z 72.

The insoluble fraction of cylinder 2 deposits from MMT fuel operation was examined by MALDI-TOF-MS. Almost no peaks are seen in the m/z range above 300. Four homologous series (separated by m/z 14) were prominent in the m/z range of 100 to 300, with many homologous series visible slightly above the base line. These four series have maxima at m/z 258, 248, 184, and 158. MS/MS of the ion at m/z 248 (248.16) shows prominent peaks at m/z 216, 156, and 142.

The IR results indicate both fractions have high concentrations of carbonyl functionality. The MS of the soluble fraction indicates possible C bonded to O species. However, N species can not be ruled out.